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Research during the last three years has focused on using negative ion photoelectron (PE) spectroscopy and zero electron kinetic energy (ZEKE) spectroscopy to probe the effects of clustering on the energetics, spectroscopy, and dynamics of ions and transition states, and to investigate the ground and excited electronic states of reactive free radicals. We have also developed a new spectroscopic method in which stimulated Raman pumping combined with PE spectroscopy is used to measure vibrational frequencies in negative ions. Results are summarized in more detail below.

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Abstract:

Research during the last three years has focused on using negative ion photoelectron (PE) spectroscopy and zero electron kinetic energy (ZEKE) spectroscopy to probe the effects of clustering on the energetics, spectroscopy, and dynamics of ions and transition states, and to investigate the ground and excited electronic states of reactive free radicals. We have also developed a new spectroscopic method in which stimulated Raman pumping combined with PE spectroscopy is used to measure vibrational frequencies in negative ions. Results are summarized in more detail below.

1) *PE and ZEKE spectroscopy of clustered halide ions*

We have measured the ZEKE spectrum of diatomic ArCl⁻, and observed transitions to the X1/2 ground state and the low lying I3/2 and II1/2 states of neutral ArCl.[1] The resolution in these spectra is around 1 cm⁻¹, enabling us to resolve vibrational progressions involving the low frequency anion (29 cm⁻¹) and neutral (14-18 cm⁻¹) vibrations. Analysis of these spectra yielded the first high quality experimental potential for the negative ion, showing that the anion well depth is substantially less than that extracted from ion mobility data[2] (65 meV vs. 104 meV), and that the anion bond length is much longer (3.71 vs. 3.14 Å). Similar experiments[3] on XeCl⁻ also yield an accurate anion potential that is at odds with earlier ion mobility data.

The ArCl⁻ diatomic data was then used to analyze the ZEKE spectrum of polyatomic Ar_nCl^- clusters (n=2-15).[4] The shifts in the electron affinities (EA's) in those spectra as a function of cluster size were compared to simulated annealing calculations incorporating the diatomic anion and neutral potentials as well as non-additive terms in the anion and neutral clusters. In the absence of non-additive terms, the calculated EA's were too high by as much as 1500 cm⁻¹. The two major non-additive terms needed to yield good agreement with experiment were the expulsive many-body induction and the attractive charge-exchange quadrupole interactions, both of which occur only in the anion cluster. The EA's show a clear shell-closing at n=12, corresponding to an icosahedral arrangement of Ar atoms around the Cl⁻ anion.

The PE spectra of Xe_nI^- (n≤13) clusters[5] were measured in order to resolve discrepancies in the electron affinities between an earlier, lower resolution PE study by Becker[6] and our previous ZEKE spectra[7] of these clusters. The ZEKE spectra yielded considerably lower EA's than the PE spectra by as much as 80 meV for the n=12 cluster. Our new PE spectra yield EA's intermediate between the two experiments. Although the

anions are closed shell species, their spectroscopy is complicated by the existence of charge-transfer-to-solvent (CTTS) excited states that lie just below the electron detachment threshold.[8] These states distort the ZEKE spectra for the larger clusters, yielding artificially low apparent electron affinities that reflect the positions of the CTTS states rather than the detachment thresholds. On the other hand, the earlier PE spectra appeared to suffer from calibration errors and yielded EA's that were too high. Our spectra confirm a shell-closing at n=12, similar to that seen for Ar_nCl^- clusters.

We also measured the anion photoelectron spectra of $I_2^-(CO_2)_n$ clusters (n = 1-8) at a photon energy of 4.661 eV.[9] The experiment yielded size-dependent vertical and adiabatic detachment energies for the formation of the ground state and low-lying valence-excited states of the neutral cluster. Vertical detachment energies were successively blue-shifted with increasing cluster size, indicating a stronger stabilization of the anionic cluster relative to the neutral counterpart. In addition, a short progression in the CO_2 bending mode was observed in the n=1 and 2 clusters, indicating that the CO_2 solvent species are slightly bent (~2.5°) in the anion clusters.

2) *Transition state spectroscopy in clusters*

We demonstrated several years ago that photoelectron spectroscopy of stable negative ions could be used to probe the transition state of neutral bimolecular reactions, provided that the anion and transition state geometries were similar.[10] Bihalide anions such as IHI^- and $BrHI^-$ were shown to be particularly suitable transition state precursors.[11-13] We recently measured photoelectron spectra of $BrHI^-(Ar)$ and $IHI^-(Ar)_n$ (n=1-15) in order to investigate the effect of stepwise solvation on transition state spectroscopy and dynamics.[14,15]

Our PE spectra of $BrHI^-(Ar)$ and $IHI^-(Ar)$ showed that even a single weakly bound solvent species such as Ar induced significant changes in the photoelectron spectrum of the bare anion.[15] These changes are primarily due to cooling effects, since a

cluster in which an Ar atom is clustered to a vibrationally excited bihalide anion will undergo predissociation before it passes through our mass spectrometer, leaving only those clusters in which the anion chromophore is vibrationally cold; similar effects have been seen in the PE spectrum of $I_2^-(Ar)$ and in the infrared spectrum of clustered halide anions.[16,17] As a consequence, the vibrational features in the BrHI$^-$(Ar) PE spectrum are considerably narrower than in the BrHI$^-$ spectrum,[13] enabling a more detailed comparison with theory. While the bare IHI$^-$ spectrum shows a well-resolved progression in the relatively high frequency IHI antisymmetric stretch,[11] the IHI$^-$(Ar) PE spectrum shows additional structure from progressions in low frequency hindered rotor states of the IHI complex.

The PE spectra of IHI$^-$(Ar)$_n$ (n=1-15) clusters show several trends of interest.[14] The shifts with EA as a function of cluster size are very similar to those seen for $I_2^-(Ar)_n$ clusters,[16] implying that the first six Ar atoms cluster around the waist of the IHI$^-$, where they can interact with the partial negative charges on the two I atoms. Subsequent Ar atoms bind primarily to a single I atom. We also observe a change in the spacing of the IHI antisymmetric stretch frequency as a function of cluster size, an effect attributed to solvent-induced distortion of the IHI$^-$ geometry. Finally, the low-frequency hindered rotor structure seen in the binary IHI$^-$(Ar) cluster becomes more pronounced for the largest clusters we studied. This effect is counterintuitive, because clustering generally obscures vibrational structure in PE spectra. We attribute it to caging of the neutral IHI complex by the surrounding Ar atoms, resulting in a longer lifetime and hence sharper structure than seen in the smaller clusters. This effect, represents a remarkable demonstration of the effect of clustering on transition state dynamics.

3) *Characterization of free radicals by anion PE spectroscopy*

Our photoelectron spectrum of I_3^- provided the first experimental observation of the I_3 radical and showed it to be a bound species that is nearly linear and

centrosymmetric,[18] a result supported by recent electronic structure calculations.[19] Continuing in this vein, we have measured the photoelectron spectrum of Cl_3^- at 193 nm.[20] Several electronic bands are observed but no vibrational structure is resolved. Electronic structure calculations by Morukuma[21] indicate that while Cl_3^- is a strongly bound species with $D_{\infty h}$ symmetry, Cl_3 is at best a weakly bound, asymmetric van der Waals complex of the form $Cl\cdot\cdot Cl_2$. Photodetachment of Cl_3^- therefore appears to access the transition state of the $Cl + Cl_2$ exchange reaction rather than a Cl_3 minimum. The positions of the bands in the experimental PE spectrum are in reasonable agreement with electronic structure calculations.

We have also continued our investigations of the I_3 radical. The electronic spectroscopy and photodissociation dynamics of the I_3 radical were investigated with two experimental methods.[22] The ground and several low-lying excited states of I_3 radical were characterized by photoelectron spectroscopy of I_3^- at 213nm. In addition, photodissociation of the I_3 radical was investigated at selected photon energies by fast radical beam photofragment translational spectroscopy.[23] Two product channels were observed with mass ratios of 1:2 and 1:1, and translational energy ($P(E_T)$) distributions were measured. The $P(E_T)$ distributions for products with mass ratio 1:2 show that this channel corresponds to I_2 plus atomic I in its $^2P_{3/2}$ or $^2P_{1/2}$ state. The 1:1 channel corresponds to symmetric three-body dissociation to three I atoms, a rare observation of a concerted three-body process..

The photoelectron spectrum of the $HCCO^-$ anion was measured and analyzed by comparison with a sophisticated theoretical model that accounts for the quasi-linearity of the $\tilde{X}\,^2A''$ state of HCCO and its Renner-Teller coupling to the nearby $\tilde{A}\,^2A'$ state.[24] Because of these effects, the vibrational structure in the anion PE spectrum cannot be fit using the simple separable harmonic oscillator models that are generally used to simulate PE spectra. The spectrum could be fit reasonably well using an ab initio geometry for the

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$\tilde{X}\,^2A''$ state that was quite close to the anion geometry, a barrier to linearity of 643 cm^{-1}, and by incorporating strong coupling between the C-C and C-O stretches.

4) *Vibrational spectroscopy of negative ions using stimulated Raman pumping*

We reported the first demonstration of a technique for vibrational spectroscopy of anions, stimulated Raman pumping-anion photoelectron spectroscopy.[25] It combines the high spectral resolution of stimulated Raman pumping with the high detection efficiency, mass-selectivity, and wide applicability of anion photoelectron spectroscopy. In this experiment, anions are vibrationally excited with stimulated Raman pumping using two pulsed lasers, a fixed frequency pump laser and tunable Stokes laser. Vibrational excitation is detected through the appearance of hot bands in the photoelectron spectrum. Hence, by integrating the hot band region of the PE spectrum while scanning the Stokes laser, we observe signal only when the difference in the pump and Stokes photon energies is equal to a vibrational transition. We obtained the vibrational spectrum of a test system, C_2^-, in which we determine the frequency of the $1 \leftarrow 0$ vibrational transition to be 1757.8 ± 0.1 cm^{-1}, and have recently located the 1_0^1 transition in C_5^- at 1853 cm^{-1}.

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